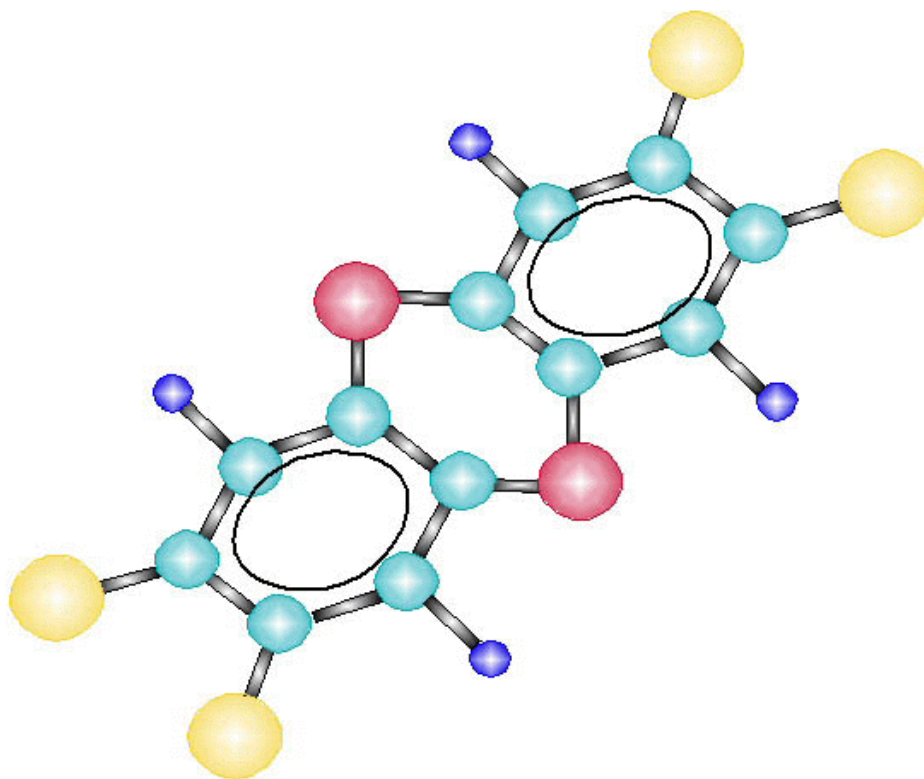


# The Use of Surrogate Compounds as Indicators of PCDD/F Concentrations in Combustor Stack Gases



# **The Use of Surrogate Compounds as Indicators of PCDD/F Concentrations in Combustor Stack Gases**

Annual Performance Measure 140  
Goal 5 Waste Management

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## **Abstract**

Emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) from stationary combustion sources are of concern due to their carcinogenicity and endocrine effects. PCDDs/Fs are typically present only in minute concentrations in combustor stack gases, which makes sampling and analysis of these compounds extremely expensive and time consuming. Direct, real-time measurement of all PCDD/F isomers of concern is not possible using current technology. It is possible, however, to estimate stack concentrations of PCDDs/Fs by measuring other indicator (surrogate) compounds that are present in the stack gases at much higher concentrations. Appropriately selected surrogate compounds would be easier to measure than PCDDs/Fs and can be measured in real-time or near real-time by stack gas monitoring technology that is currently available either commercially, or in various stages of development. This report discusses the various surrogates that can be used to indicate PCDD/F concentrations, how those surrogates can be measured, and a state-of-the-art assessment of availability and effectiveness of analyzers for measuring those compounds.

## Foreword

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Lee A. Mulkey, Acting Director  
National Risk Management Research Laboratory

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# Contents

<u>Section</u>	<u>Page</u>
Abstract .....	ii
List of Figures .....	vi
List of Tables .....	vii
Glossary .....	viii
Acknowledgments .....	x
 1.0 Introduction .....	 1-1
1.1 Emissions of PCDDs/Fs .....	1-1
1.2 Formation of PCDDs/Fs .....	1-1
1.3 Current Regulatory Approach .....	1-2
1.4 Sampling and Analytical Methods .....	1-3
1.5 Surrogate Concept .....	1-4
2.0 Surrogate Approaches .....	2-1
2.1 Measurement of Carbon Monoxide .....	2-1
2.2 Measurement of Total Hydrocarbons .....	2-2
2.3 Measurement of Volatile Organic Compounds .....	2-3
2.4 Measurement of Chlorobenzenes and Chlorophenols .....	2-6
2.5 Measurement of Polychlorinated Biphenyls .....	2-9
2.6 Measurement of Polycyclic Aromatic Hydrocarbons .....	2-9
2.7 Measurement of Lower Chlorinated Dioxins and Furans .....	2-10
3.0 Surrogate Analytical Techniques .....	3-1
3.1 Continuous Emission Monitors for Carbon Monoxide .....	3-1
3.2 Continuous Emission Monitors for Total Hydrocarbons .....	3-1
3.3 Continuous Emission Monitors for Volatile Organic Compounds .....	3-1
3.4 Continuous Emission Monitors for Chlorobenzenes and Chlorophenols .....	3-2
3.5 Continuous Emission Monitors for Polycyclic Aromatic Hydrocarbons .....	3-3
3.6 Continuous Emission Monitors for Lower Chlorinated Dioxins and Furans .....	3-4
4.0 Conclusions .....	4-1
5.0 References .....	5-1

## List of Figures

<u>Figure</u>	<u>Page</u>
1-1 Formation Pathways of PCDDs/Fs and Other High MW Pollutants . . . . .	1-2
1-2 Relative Concentrations of PCDDs/Fs and Their Surrogates . . . . .	1-4
2-1 CO vs. Total PCDD/F Stack Emissions in an RDF Combustor . . . . .	2-2
2-2 THC vs. Total PCDD/F Stack Emissions in an RDF Combustor . . . . .	2-3

## List of Tables

<u>Table</u>	<u>Page</u>
1-1 PCDD/F Emission Limits from Waste Combustors .....	1-3
2-1 Regression Results of C <sub>2</sub> Chloroalkenes vs. Total PCDDs/Fs .....	2-5
2-2 List of CBz and CPh I-TEQ Surrogates .....	2-8
2-3 Lower Chlorinated CDDs/Fs vs. I-TEQ .....	2-11
3-1 Techniques for Rapid Measurement of VOC PICs .....	3-2
3-2 Techniques for Rapid Measurement of CBz and Cph .....	3-3

## Glossary

Term	Definition
APCS	air pollution control system
BIFs	boilers and industrial furnaces
CBz	chlorobenzenes
CEMs	continuous emission monitors
Cl	chlorine
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
CPh	chlorophenols
DOAS	differential optical absorption spectroscopy
ESP	electrostatic precipitator
FID	flame ionization detector
FTIR	Fourier transform infrared
GC	gas chromatography
HWCs	hazardous waste combustors
IMS	ion mobility spectroscopy
I-TEQ	international toxic equivalency
MCBz	monochlorobenzene
MS	mass spectrometry
MW	molecular weight
MWCs	municipal waste combustors
NDIR	non-dispersive infrared
NITEP	National Incinerator Testing and Evaluation Program
O <sub>2</sub>	oxygen
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
PCDDs/Fs	polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans
PCNs	polychlorinated naphthalenes

## Glossary (continued)

Term	Definition
PICs	products of incomplete combustion
RCRA	Resource Conservation and Recovery Act
RDF	refuse-derived fuel
REMPI-TOF	resonance-enhanced multiphoton ionization-time of flight
SVOCs	semivolatile organic compounds
TEFs	toxic equivalency factors
TEQ	toxic equivalency
THC	total hydrocarbons
VOCs	volatile organic compounds

## **Acknowledgments**

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## 1.0 Introduction

### 1.1 Emissions of PCDDs/Fs

The emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) from incinerators and other stationary combustion devices have been of concern since they were first measured in the stack gases from municipal waste combustors (MWCs).<sup>1</sup> PCDDs/Fs have been shown to be carcinogenic and bioaccumulative and have been found in various concentrations in the exhaust gases from almost every combustion source.<sup>2</sup> Of the 75 possible isomers of PCDD and the 135 possible isomers of PCDF, the 17 isomers with chlorine (Cl) substituted at the 2,3,7, and 8 positions exhibit the carcinogenic behavior.

To account for the varying levels of toxicity of the various PCDD/F isomers, stack gas concentrations of PCDDs/Fs are frequently expressed in units of toxic equivalency (TEQs). TEQs are weighted concentration values based on a series of toxic equivalency factors (TEFs) that are estimated using various toxicological models based on in vivo or in vitro studies. Each of the 17 toxic isomers has an associated TEF, normalized so that 2,3,7,8-tetrachloro dibenzo-p-dioxin (TCDD) is defined as having a TEF of 1. The TEQ is calculated using Equation (1).

$$\text{TEQ} = \sum C_i \text{TEF}_i \quad (1)$$

where  $C_i$  represents the concentration of the  $i^{\text{th}}$  isomer (usually in ng/dscm) and  $\text{TEF}_i$  represents the TEF for the  $i^{\text{th}}$  isomer. To account for dilution, concentrations are corrected to a common oxygen ( $\text{O}_2$ ) or carbon dioxide ( $\text{CO}_2$ ) concentration, such as 7%  $\text{O}_2$ . For the purposes of this report, the International TEQ<sup>2</sup> (I-TEQ) will be used for all of the correlations between PCDDs/Fs and other pollutants except for the contribution of other chloroorganics like polychlorinated biphenyls (PCBs), which will use TEQs calculated from TEFs derived from the World Health Organization.<sup>3</sup>

### 1.2 Formation of PCDDs/Fs

Laboratory and field studies of PCDD/F formation mechanisms have resulted in theories of the chemical pathways that lead to the production of PCDDs/Fs as unwanted trace by-products from combustion devices. It is generally accepted<sup>4-6</sup> that one of the pathways involves organic

products of incomplete combustion (PICs) leaving the high temperature zones of a combustor in the form of volatile or semivolatile organic compounds (VOCs or SVOCs). These compounds, known as precursors, can undergo heterogeneous reactions with flyash-bound metallic catalysts (such as copper) in the cooler regions of the combustor, including transition ducts and the air pollution control system (APCS), such as an electrostatic precipitator (ESP), that result in the formation of PCDDs/Fs. The heterogeneous reactions are strongly dependent on the temperature and residence time within the APCS. Iino et al.<sup>7</sup> evaluated isomer distribution patterns from several waste incineration facilities and found that there was a great deal of consistency among them and suggested a mechanism that accounts for variations in the isomer patterns and subsequently the TEQs. A simplified diagram of the formation pathways of PCDDs/Fs, PCBs, polychlorinated naphthalenes (PCNs) is shown in Figure 1-1.

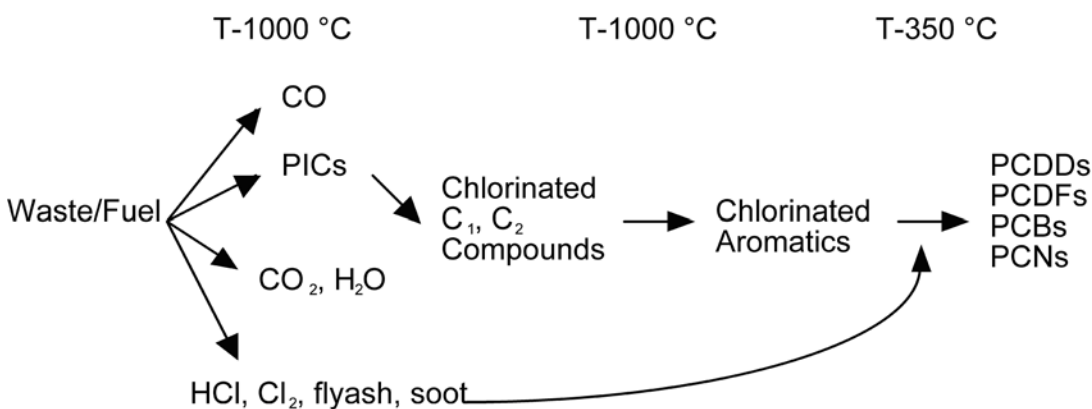


Figure 1-1. Formation Pathways of PCDDs/Fs and Other High MW Pollutants

### 1.3 Current Regulatory Approach

Emissions of PCDDs/Fs from MWCs are regulated under the Clean Air Act Amendments of 1990<sup>8</sup>. Emissions of PCDDs/Fs from hazardous waste combustors (HWCs), boilers and industrial furnaces (BIFs), including cement kilns, halogen acid furnaces, and lightweight aggregate kilns, are regulated under the Resource Conservation and Recovery Act (RCRA)<sup>9</sup>. The emission limits from hazardous and municipal waste combustion facilities are listed in Table 1-1. It is apparent from these emission limits that average day-to-day concentrations of PCDDs/Fs are exceedingly low; i.e., in the low parts-per-trillion (ppt) range.

Table 1-1. PCDD/F Emission Limits from Waste Combustors

Facility Type	PCDD/F Emission Limit (corrected to 7% O <sub>2</sub> )
Municipal Waste Combustors	13 ng/dscm total mass (mandatory) or 7 ng/dscm total mass (optional to qualify for less frequent testing) <sup>10</sup>
Hazardous Waste Combustors	0.2 ng TEQ/dscm or 0.4 ng TEQ/dscm if particulate matter APCD inlet temperature <400 °F

## 1.4 Sampling and Analytical Methods

Due to the low stack gas concentrations of the target analytes, sampling and analysis for PCDDs/Fs is a complicated, labor-intensive, and expensive process. Using EPA Method 23A<sup>11</sup>, an isokinetic sample is drawn from the stack, usually for several hours, using an extractive sampling probe, a heated filter, an XAD-2 resin trap, and a series of impingers. This sampling train is then broken down and recovered, yielding filters, XAD-2 resin, and various rinsates.

The recovered samples are then brought to an analytical laboratory where a series of extraction and cleanup procedures are performed and the samples are eventually analyzed by gas chromatography (GC) and mass spectrometry (MS). If a high resolution GC/MS system is used, then the analysis is described in EPA Method 8290<sup>12</sup>; if a low resolution GC/MS system is used, then the analysis is described in EPA Method 8280A<sup>13</sup>. Analytical costs are typically in the range of \$1000 per sample.

Since triplicate samples are typically required for compliance testing,<sup>9</sup> it usually requires a sampling team to be in the field for a week or two for a single stack test. These stack tests are done periodically depending on the requirements of the permitting authority. During the periods when stack sampling is not occurring, facilities typically are required to maintain operations within a specified window defined by other indirect parameters such as temperature, O<sub>2</sub> or carbon monoxide (CO) concentrations defined during compliance testing or trial burns.

Because of the time and expense involved in sampling for PCDDs/Fs, it is not practical to perform system optimizations to minimize emissions of PCDDs/Fs. In addition, no indication is available as to the temporal variability of PCDD/F emissions due to operational fluctuations.

The standard analytical methods for PCDD/F only measure the tetra- through octa-chlorinated isomers because, from a regulatory standpoint, only the isomers with chlorine substituted at the 2,3,7,8- positions are useful. Recently, however, expanded methods have been made available

that analyze for the mono-, di-, and tri-substituted CDDs and CDFs for purposes of aiding in the understanding of the PCDD/F formation mechanisms.

## 1.5 Surrogate Concept

It would be ideal if all of the toxic PCDD/F isomers could be measured continuously in real-time. However, current state-of-the-art instrumentation is not capable of achieving this goal. Instead, other more easily-measurable parameters can be used to give an indication of the concentrations of PCDDs/Fs in the stack gases. These more easily measurable compounds are called surrogates. Figure 1-2 elaborates on the earlier PCDD/F formation pathway figure by describing the concentrations of the intermediate species that can be found in the stack gases and are important in the PCDD/F formation mechanism. The main problem from a practical standpoint is that the higher concentration and subsequently more easily measurable surrogate compounds are less directly involved in the mechanism that forms PCDDs/Fs.

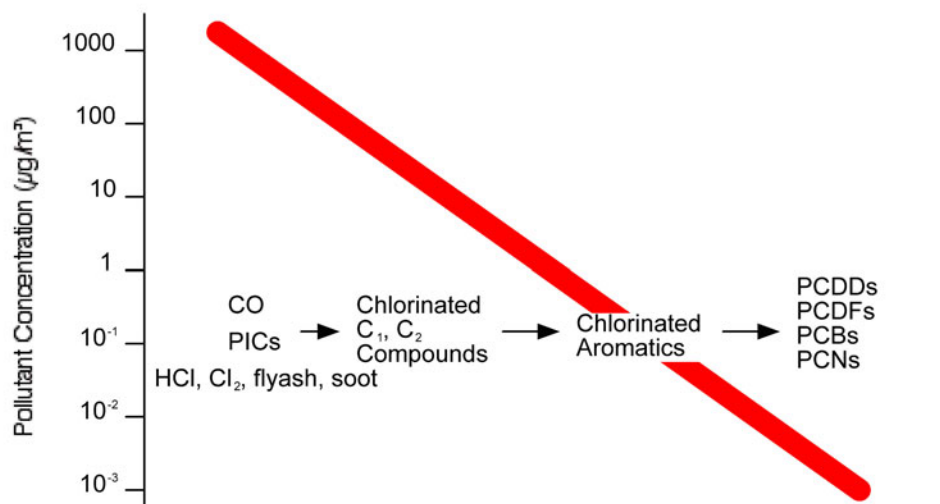


Figure 1-2. Relative Concentrations of PCDDs/Fs and Their Surrogates

The purposes of this document are as follows:

- To discuss current approaches and their limitations for using surrogates,
- To discuss what other options exist for using surrogate indicators of PCDDs/Fs,
- To discuss methods for continuously or semi-continuously measuring those surrogate compounds, and
- To discuss the timeline of commercial availability of those various analytical techniques.

## 2.0 Surrogate Approaches

A surrogate parameter can be a single pollutant that can itself, or in combination with other parameters, account for the variability of the PCDD/F data. A linear relationship between the surrogate and the PCDDs/Fs, derived using linear least squares fitting, would be the simplest use of a surrogate. However, given that minor changes in operational parameters can result in orders of magnitude changes in the concentrations of PCDDs/Fs, it is likely that the most effective surrogates will probably exhibit a non-linear relationship with PCDDs/Fs, such as a log-linear relationship. Multiple parameter models can improve the overall fit, although given the general lack of highly robust PCDD/F vs. operational conditions data sets, adding too many parameters to the model can result in simply re-predicting the original data set as opposed to elucidating the statistical relationship between the surrogate and the PCDD/F. In addition, multiparameter models can become counter intuitive due to competing effects of individual parameters, and they are difficult to visualize on paper. For the purposes of this report, statistical significance is defined as when the “P value” of the parameter is less than 0.05. In addition, the correlation coefficients used will be the  $R^2$  value.

For the purposes of this report, the following potential surrogate PCDD/F indicators will be discussed:

- □ Carbon Monoxide,
- □ Total Hydrocarbons (THC)
- □ Low Molecular Weight (MW) VOCs,
- □ Chlorobenzenes (CBz) and Chlorophenols (CPh),
- □ PCBs,
- □ Polycyclic Aromatic Hydrocarbons (PAHs), and
- □ Lower Chlorinated Dioxins and Furans.

### 2.1 Measurement of Carbon Monoxide

CO is commonly used as an indicator of poor combustion and is relatively easy to measure using non-dispersive infrared (NDIR) continuous emission monitors (CEMs). Stack CO concentrations are typically limited to a maximum hourly rolling average in many combustion facility permits and are typically found at levels between 1 and 100 ppmv in well operated combustors. During the National Incinerator Testing and Evaluation Program (NITEP) that was performed collaboratively between the U.S. EPA and Environment Canada during the late

1980s and early 1990s,<sup>14</sup> analyses were performed at a variety of combustion conditions to see if CO could be an effective surrogate for PCDDs/Fs in the stack gases of municipal waste combustion facilities. It was found that CO was a good indicator of PCDD/F concentrations when the facility was operating poorly; however, for a well-operated facility, CO was not a good indicator of PCDDs/Fs. Figure 2-1 illustrates the CO emissions vs. total PCDDs/Fs at a variety of combustion conditions from a refuse-derived fuel (RDF) combustor. Observe how PCDD/F tracks CO for conditions where CO emissions are high, but there is no apparent trend in the region of the plot where CO emissions are low. This suggests that low CO emissions are a necessary condition to minimize PCDDs/Fs but are not sufficient to assure compliance. This observation is also supported in later work by German researchers.<sup>15</sup>

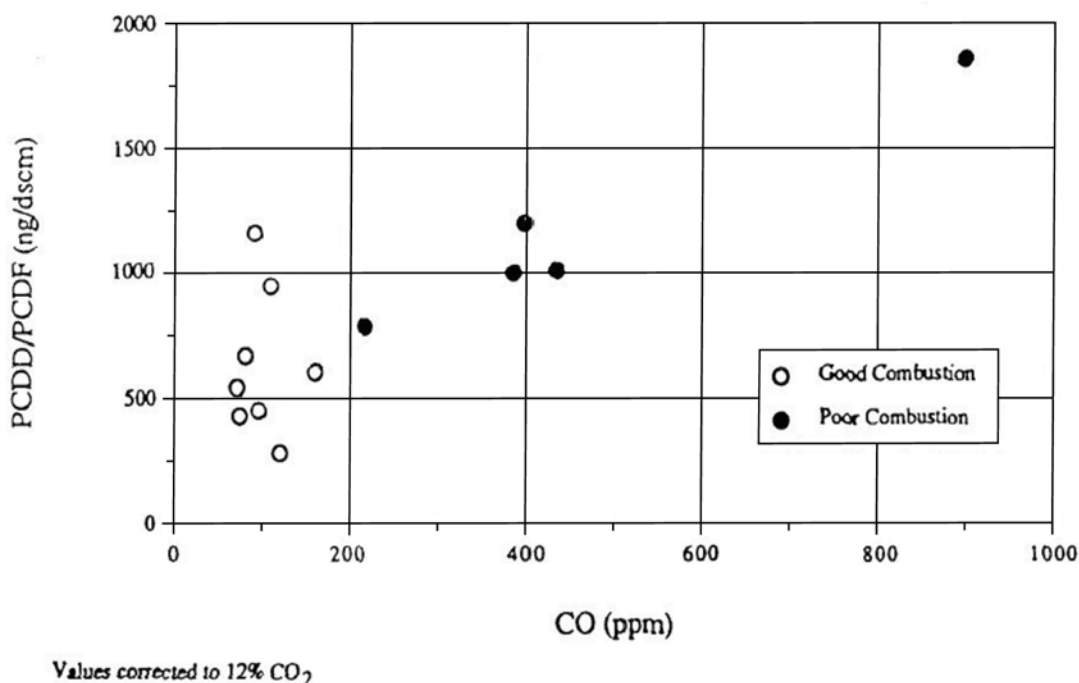


Figure 2-1. CO vs. Total PCDD/F Stack Emissions in an RDF Combustor<sup>14</sup>

## 2.2 Measurement of Total Hydrocarbons

Similarly, THC is another parameter that is frequently measured at combustion facilities to assure good combustion and is fairly easy to measure using flame ionization detector- (FID) based CEMs, either heated or unheated. THC concentrations are typically in the 1 to 10 ppmv range for a well operated combustion facility. THC results are reported in units of methane or propane equivalents depending on how the CEM was calibrated. THC was also evaluated as a potential surrogate for PCDDs/Fs during the NITEP testing program. Conclusions were drawn

similar those for using CO for a PCDD/F surrogate; low THC is a necessary condition to assure low PCDD/F emissions, but low THC is not a sufficient condition to assure compliance for a well operated facility. Figure 2-2 shows THC vs. total PCDD/F emissions from the stack of an RDF combustor.

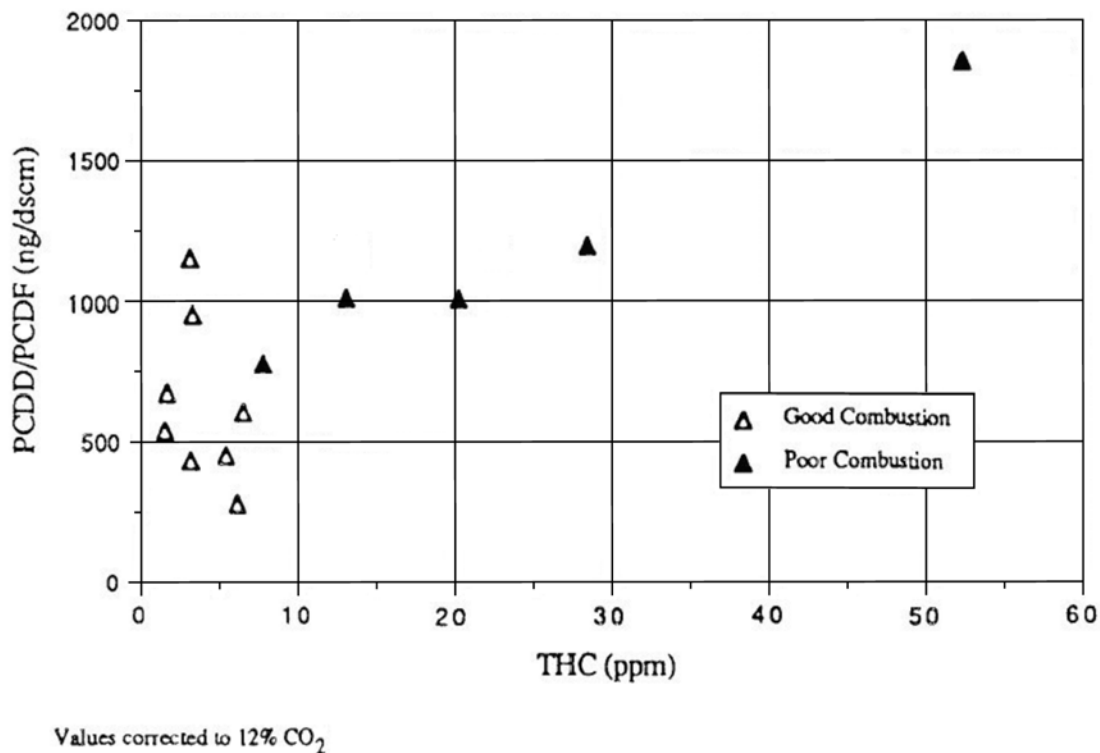


Figure 2-2. THC vs. Total PCDD/F Stack Emissions in an RDF Combustor<sup>14</sup>

### 2.3 Measurement of Volatile Organic Compounds

The measurement of low molecular weight VOC PICs and their application as a potential surrogates for PCDD/F emissions adds another level of complexity to the problem of finding a suitable surrogate. VOC PIC concentrations are typically 1 to 100  $\mu\text{g}/\text{m}^3$  in a well operated combustion facility; these concentrations are approximately 3 orders of magnitude lower than the concentrations at which CO and THC are typically found. However, some low molecular weight PICs are believed to be crucial intermediates in the chemical reaction mechanisms that waste undergoes as it combusts. In particular, C<sub>1</sub> and C<sub>2</sub> chloroorganics such as vinyl chloride, chloromethane, dichloromethane, trichloroethylene, tetrachloroethylene, and their radicals are important species.<sup>6</sup> These species are directly involved in aromatic ring growth reactions that

may eventually result in formation of PCDDs/Fs. Since these species are formed in the high temperature regions of the combustor and the PCDDs/Fs are formed in the lower temperature zones, it is likely that VOC PICs would require a temperature parameter such as an exhaust duct temperature, stack temperature, or quench rate to correlate effectively with PCDDs/Fs.

Lemieux et al. analyzed three data sets from a pilot-scale incineration facility to evaluate potential correlations between C<sub>2</sub> VOC PICs and total PCDDs/Fs.<sup>16</sup> Test conditions ranged over a fairly wide set of variations, including different surrogate wastes containing varying amounts of bromine and chlorine. In these datasets, total PCDDs/Fs were available but not I-TEQ; also many of the potential VOC PIC indicators were present at concentrations at or near the instrument (an online GC) detection limits, which significantly reduced the available data with which to develop correlations. Out of the 10 C<sub>1</sub> and C<sub>2</sub> target analytes of the online GC, only 5 (vinyl chloride, 1,1-dichloroethene, 1,2-dichloroethene, trichloroethylene, and tetrachloroethylene) were consistently present at quantifiable levels in all the data sets. Statistical analyses were performed, both on individual data sets and on the data set derived from combining all three individual sets of data. Each data set contained one or more C<sub>2</sub> chloroalkenes that were able to account for a statistically significant fraction of the variance in PCDD/F emissions.

For each individual set of data, simple linear regressions were generated between individual C<sub>2</sub> chloroalkenes and the total PCDDs/Fs. Variations in the vinyl chloride concentrations were able to account for the variations in the PCDD/F concentrations strongly in two of the three data sets and weakly in the other. A regression on the combined data set showed a significant ( $R^2 = 0.582$ ) relationship between vinyl chloride (log) concentrations and PCDD/F concentrations. Performing a two-parameter regression by combining one temperature-related parameter with a C<sub>2</sub> chloroalkene concentration-related parameter yielded statistical models that were able to account for more of the variance in PCDD/F concentrations. In the referenced paper,<sup>16</sup> several temperature parameters were evaluated, and the quench rate (the rate at which the duct temperature dropped from the furnace exit to the sampling location) was found to yield the best two-parameter fits. Again, vinyl chloride and other C<sub>2</sub> chloroalkene-related parameters exhibited statistical significance as well, including the total concentration of all C<sub>2</sub> chloroalkenes. The advantage of choosing a single C<sub>2</sub> chloroalkene to serve as an indicator is that available measurement techniques are much less expensive when directed at a more limited target analyte set. A limitation of using this technique is that the C<sub>2</sub> chloroalkene must be measured prior to any VOC removal device. Some combustion devices utilize carbon adsorption systems to remove organic compounds from stack gases in the APCS, which would require that the chloroalkenes be measured upstream of the carbon bed as opposed to inside the

stack. In other words, the pre-APCS VOC concentrations would need to correlate with PCDDs/Fs in the stack. Overall, it appears that concentrations of C<sub>2</sub> chloroalkenes, when coupled with a temperature related parameter, may have good potential as a surrogate indicator of PCDDs/Fs, provided sufficient detection limit goals are met. Table 2-1 lists the results of using low MW VOC PICs as a surrogate for PCDDs/Fs; the results with statistical significance are shown.

Table 2-1. Regression Results of C<sub>2</sub> Chloroalkenes vs. Total PCDDs/Fs<sup>16</sup>

No. of Model Parameters	Data Set	Parameter(s)	R <sup>2</sup>
1	1	1,2-Dichloroethene	0.633
		Trichloroethylene	0.615
	2	Vinyl Chloride	0.287
	3	Vinyl Chloride	0.681
		1,1-Dichloroethene	0.436
		1,2-Dichloroethene	0.452
		Tetrachloroethylene	0.773
	Combined	Vinyl Chloride	0.582
		1,1-Dichloroethene	0.162
		1,2-Dichloroethene	0.476
		Tetrachloroethylene	0.236
		Σ C <sub>2</sub> chloroalkenes	0.282
2	Combined	Vinyl Chloride + Quench Rate	0.677
		1,1-Dichloroethene + Quench Rate	0.399
		1,2-Dichloroethene + Quench Rate	0.589
		Trichloroethylene + Quench Rate	0.302
		Tetrachloroethylene + Quench Rate	0.645
		Σ C <sub>2</sub> chloroalkenes + Quench Rate	0.673

Based on this information, the following observations can be made about using low MW VOC PICs as a surrogate for PCDDs/Fs:

- □ Low MW VOC PICs may be useful as PCDD/F indicators, but a temperature-related parameter such as a flue gas temperature, stack temperature, or quench rate should be included in the correlation to improve the fit.
- □ Instrument detection limits of 1 ppbv may not be sufficient to allow development of correlations between low MW VOCs and PCDDs/Fs.

- □ The data used for comparison were all taken on a single facility using different fuels and conditions; this suggests that low MW VOCs may have potential across different fuel types, but it is unknown how the correlations hold from facility to facility.

## 2.4 Measurement of Chlorobenzenes and Chlorophenols

Current knowledge of the formation mechanism of PCDDs/Fs in incinerators proposes that condensation reactions of chlorinated aromatic compounds such as CBz and CPh may be responsible for a significant amount of the PCDDs, and possibly the PCDFs, formed in the lower temperature regions of waste combustors.<sup>2</sup> As such, it would be logical that the concentrations of PCDDs/Fs in the stack would be a function of the concentrations of CBz and CPh at some point in the combustor. A potential drawback of the use of CBz and CPh as a surrogate for PCDDs/Fs is that the concentrations of CBz and CPh in a well operated waste combustor are fairly low, typically in the range of 1 to 10  $\mu\text{g}/\text{m}^3$ —about an order of magnitude lower than the low molecular weight VOC PICs.<sup>15</sup> Another potential drawback is that many of the CBz isomers and all of the CPh isomers are semi-volatile compounds, have fairly high boiling points, and are typically associated with particulate matter at stack temperatures as opposed to being in the gas-phase. In addition, CPh are fairly reactive and can chemisorb onto surfaces in the APCS. Only monochlorobenzene and dichlorobenzene can be measured using the standard EPA method for VOCs;<sup>17-19</sup> the standard method for semivolatile compounds<sup>20</sup> requires extensive laboratory preparation (extraction, concentration) prior to analysis.

There has been extensive work performed in Germany examining the relationships between PCDD/F in the flue and stack gases and concentrations of various chlorinated aromatic compounds. Kaune et al.<sup>15</sup> initially examined field data from a rotary kiln hazardous waste combustion facility equipped with a heat recovery boiler, dry ESP, condenser, then a wet ESP. They found relatively poor correlations between CPh and PCDDs/Fs because the extremely low concentrations of the CPh made it difficult to develop good fits. However, correlations were successfully developed between pentachlorobenzene ( $\text{Cl}_5\text{Bz}$ ) and various PCDD/F homologue groups in the flue gases, individual toxic isomers, total PCDDs/Fs, and I-TEQ. In particular, a correlation with  $R^2=0.94$  was found between  $\text{Cl}_5\text{Bz}$  and I-TEQ at an intermediate location within the flue gas cleaning system. It must be noted that for the test series in question, the concentrations of the PCDDs/Fs varied over 2 orders of magnitude, as did the concentrations of CBz.

A follow-on study at the same incinerator<sup>21</sup> showed that varying operation of the flue gas cleaning system by altering injection rates of activated carbon did not result in failure of the ability of  $\text{Cl}_5\text{Bz}$  to still yield good correlations with I-TEQ. Further work by the same

investigator<sup>22</sup> showed that the sum of the tetrachlorobenzene ( $\text{Cl}_4\text{Bz}$ ) isomers also yielded good correlations ( $R^2=0.894$ ) with I-TEQ. They were not able to find any correlation in the stack gases.

Further work by the same investigators<sup>23</sup> examined data from three different incinerators of slightly different designs and several different sampling points within the incinerators. They found that the data points from the different facilities either fell on the same regression line or on parallel regression lines that differed only by their intercept. This suggested that the slope of the regression line for a facility that has not been investigated could be taken from correlations developed at a similar sampling point of an already-investigated incinerator. This would significantly reduce the workload and cost necessary to develop detailed regression equations.

Some researchers in Finland<sup>24</sup> examined correlations between gas-phase and particulate-bound chlorinated aromatic compounds and PCDDs/Fs and found that gas-phase indicator compounds gave good correlations whereas particulate-phase compounds did not. This observation is an important implication when on-line measurement of these compounds is concerned, since the most promising on-line measurement methods all involve measurement of gas-phase compounds only.

All of the above CBz and CPh measurements were made using conventional extractive sampling techniques. Ideally, the surrogates would be measured in real time or near-real time in order to be useful for system optimization and to minimize the cost of their application. Further work has been done on one of the same three German incinerators using an on-line technique—resonance enhanced multiphoton ionization-time of flight (REMPI-TOF) mass spectrometry—in which chlorinated aromatics were measured in real time and compared to extractively collected PCDD/F measurements.<sup>25</sup> In these tests, monochlorobenzene (MCBz) was measured in real time at two locations in the incinerator: the boiler exit and the stack. The investigators found a relationship between MCBz measured in the flue gas and I-TEQ at the boiler exit with an  $R^2=0.82$  and at the stack exit with an  $R^2=0.76$  using the same regression methodology. This suggests that measurements of some compounds such as MCBz in higher temperature regions of the combustor, where they are mainly in the gas-phase, can be useful predictors of I-TEQ in the stack, where those compounds may be partially in the solid-phase (and thus inaccessible to gas-phase measurement techniques like REMPI-TOF).

In a separate paper,<sup>26</sup> principal component analysis was performed on various CBz isomers to see which ones tracked I-TEQ best. They found that MCBz, 1,3-dichlorobenzene ( $1,3\text{-Cl}_2\text{Bz}$ ),

1,2-dichlorobenzene (1,2-Cl<sub>2</sub>Bz), and Cl<sub>5</sub>Bz (as reported earlier<sup>15</sup>) all gave good correlations with I-TEQ. More importantly, it was found that the isomer pattern of CBz and PCDD/F did not significantly change as the flue gases passed through the APCS, which strengthens the argument that measurement of chlorinated aromatics are a robust indicator of PCDD/F concentrations. Additional work on a pilot-scale waste combustor<sup>27</sup> further strengthened the usefulness of lower chlorinated CBz as indicators of PCDD/F.

Table 2-2 lists the CBz and CPh compounds that have yielded statistically significant correlations with I-TEQ.

Table 2-2. List of CBz and CPh I-TEQ Surrogates

Compound	Approximate Concentration <sup>28</sup> (pptv)	Correlation Coefficient, R <sup>2</sup>	Source
MCBz	300	0.72	[28]
1,2-Cl <sub>2</sub> Bz	50	0.61	[28]
1,4-Cl <sub>2</sub> Bz	30	0.42	[28]
1,2,3-Cl <sub>3</sub> Bz	20	0.58	[28]
1,2,3,4-Cl <sub>4</sub> Bz	30	0.83	[28]
S Cl <sub>4</sub> Bz	NA <sup>a</sup>	0.89	[22]
Cl <sub>5</sub> Bz	10	0.62	[28]
Cl <sub>6</sub> Bz	5	0.55	[28]
2,4-Cl <sub>2</sub> Ph	50	0.64	[28]
2,4,6-Cl <sub>3</sub> Ph	30	0.67	[28]
2,3,4-Cl <sub>3</sub> Ph	10	0.41	[28]
2,3,5,6-Cl <sub>4</sub> Ph	5	0.48	[28]
2,3,4,6-Cl <sub>4</sub> Ph	5	0.56	[28]
Cl <sub>5</sub> Ph	10	0.62	[28]
	NA	0.94	[15]

<sup>a</sup> NA=not available

Based on these sources of information, the following observations can be made concerning the use of chlorinated aromatic compounds as surrogates for PCDDs/Fs:

- Sampling of the indicator compounds and PCDDs/Fs does not necessarily need to be performed at the same location to develop the correlations. This is an important point, especially as the discussion of potential measurement methodologies comes into play.

- The development of the correlations is likely to be facility-specific, although information acquired during the development of detailed regression correlations at one facility may be used successfully at other similar facilities to reduce the cost and workload of developing correlations at those facilities.
- The ability of the surrogates to predict PCDD/F concentrations improves when a wider range of concentrations is used to develop the correlations.
- In developing the facility-specific correlations, individual isomers should be considered as surrogates as well as homologue groups and entire classes of compounds.
- Developing correlations using simultaneous measurements of CBz, CPh, and PCDDs/Fs may not be useful to assure compliance; however, it may be extremely useful to allow facilities to optimize operation to minimize PCDD/F emissions.

## 2.5 Measurement of Polychlorinated Biphenyls

PCBs are believed to be formed through a set of reactions similar to those that form PCDDs/Fs. The TEQs from PCBs (calculated using TEFs published by the World Health Organization<sup>3</sup>) in waste combustors typically only represent a small fraction (less than 5%) of the PCDD/F-derived I-TEQ.<sup>29</sup> It may be possible to infer concentrations of PCDDs/Fs from total PCB concentrations or from concentrations of individual congeners.<sup>15</sup> In Kaune et al.,<sup>15</sup> it was found that heptachlorobiphenyls (Cl<sub>7</sub>B) gave an R<sup>2</sup>=0.87 correlation with I-TEQ, and individual PCB congeners may give good correlations with I-TEQ. However, PCBs are typically found in concentrations similar to PCDDs/Fs, and measurement of PCBs is typically done using the same stack gas sampling and analysis methods as is done with measurement of PCDDs/Fs, so the usefulness of PCBs as a surrogate indicator of PCDDs/Fs is highly questionable.

## 2.6 Measurement of Polycyclic Aromatic Hydrocarbons

Since PAHs are formed as a result of incomplete combustion in the furnace and are present typically in concentrations two orders of magnitude higher than PCDDs/Fs, they may be worth investigating as potential PCDD/F indicator compounds. Kaune et al.<sup>15</sup> found that fluoranthene, pyrene, benzo[ghi]fluoranthene/benzo[c]phenanthrene, chrysene, and total PAH gave correlation coefficients of 0.76, 0.76, 0.73, 0.71, and 0.84 vs. I-TEQ, respectively, at one sample point. However, no correlation was found at any of the other sample points, which suggests that the correlations of PAHs vs. PCDDs/Fs are not as robust as the correlations with the single ringed chlorinated aromatic compounds. Blumenstock et al.<sup>27</sup> used principal component analysis and found that PAHs were more closely correlated with CO emissions than with PCDD/F emissions. This suggests that PAHs, like CO, are useful indicators of whether a combustor is operating well or poorly, but may not be useful as an indicator of PCDDs/Fs.

## 2.7 Measurement of Lower Chlorinated Dioxins and Furans

Regulatory compliance sampling for PCDDs/Fs has typically only evaluated emissions of the tetra- through octa-chlorinated PCDD/F isomers, since the toxic isomers all have a minimum of four chlorines substituted at the 2, 3, 7, and 8 positions on the CDD/F molecule. Recently, though, the analytical techniques have expanded to include the mono-, di-, and tri-chlorinated CDD/F molecules due to their promise as useful indicators of PCDD/F concentrations and I-TEQ.<sup>30,31</sup> The advantages afforded by the lower chlorinated CDDs/Fs include:

- They are present typically at higher concentrations than the higher chlorinated congeners, although they are still present in very low concentrations—on the order of 1–10 ng/m<sup>3</sup> in a well operated combustion facility;
- Because of their higher volatility than the higher chlorinated PCDD/F congeners, a higher fraction of the lower chlorinated congeners are present in the gas-phase at flue- and stack-gas conditions; and
- Because of their lower numbers of substituted chlorines, they have better detection limits when measured by on-line methods such as REMPI-TOF.

Work by Oser et al.<sup>31</sup> has developed the concept of using lower chlorinated CDD/F isomers as indicators of I-TEQ. Jet-REMPI, a variant on REMPI-TOF where a supersonic jet is used to cool the gas sample to temperatures approaching absolute zero, has been used to dramatically increase the sensitivity of the REMPI-TOF method to successfully measure these compounds.

Blumenstock et al.<sup>28</sup> used REMPI-TOF on a German hazardous waste combustor to measure various MCDD/F, DCDD/F, and TriCDD/F isomers and the sum of their homologue groups and examine the statistical significance of using them to account for I-TEQ. They found that, for the plant on which they made the measurements, several of the lower chlorinated CDD isomers, and one of the lower chlorinated CDF isomers gave statistically significant correlations. Gullett and Wikström compared the lower chlorinated CDD/F isomers and homologue groups to the total PCDD/F and I-TEQ for three different datasets: one from a full-scale RDF combustor firing various mixtures of municipal waste and coal, and two from a pilot-scale research combustor burning solid fuel pellets. They developed single-, two-, and three- parameter statistical models to develop lower chlorinated CDD/F indicator relationships with both total PCDDs/Fs and I-TEQ. A summary of the results from those two studies (limited to correlations with I-TEQ) is shown in Table 2-3.

Table 2-3. Lower Chlorinated CDDs/Fs vs. I-TEQ

Number of Model Parameters	Compound(s)	Correlation Coefficient, R <sup>2</sup>	Source
1	1,3-DiCDD	0.38	[28]
	1,4,7-TriCDD	0.53	[28]
	1,2,3-TriCDD	0.55	[28]
	1,7,8-TriCDD	0.56	[28]
	1,4,6-TriCDD	0.56	[28]
	1,2,6-TriCDD	0.58	[28]
	1,2,9-TriCDD	0.52	[28]
	1,2,3-TriCDF	0.68	[30] (Norfolk data set)
		0.44	[30] (Umeå-1 data set)
		0.44	[30] (Umeå-2 data set)
	2,4,6-TriCDF	0.52	[28]
	Σ TriCDD	0.95	[30] (Umeå-2 data set)
	Σ TriCDF	0.77	[30] (Norfolk data set)
2	1,2,3-TriCDF, 1,6-DiCDD	0.84	[30] (Norfolk data set)
	1,2,3-TriCDF, 2,4,6-TriCDF	0.83	[30] (Umeå-1 data set)
		0.86	[30] (Umeå-2 data set)
	Σ DiCDF, Σ TriCDF	0.81	[30] (Norfolk data set)
	Σ TriCDD, Σ DiCDF	0.97	[30] (Umeå-2 data set)
3	Σ DiCDD, Σ DiCDF, Σ TriCDF	0.87	[30] (Norfolk data set)
		0.99	[30] (Umeå-2 data set)

## **3.0 Surrogate Analytical Techniques**

### **3.1 Continuous Emission Monitors for Carbon Monoxide**

The measurement of CO in combustor stacks using NDIR CEMs is a reliable, proven method that has been around for years.<sup>32</sup> These instruments are sensitive down to concentrations in the low parts per million range, and there are many different models that are commercially available. Most combustion facilities are required to monitor CO emissions in their stack as a requirement of their respective state's air quality permit.

### **3.2 Continuous Emission Monitors for Total Hydrocarbons**

There are two currently available technologies for the measurement of THC in combustor stacks: NDIR<sup>33</sup> and FID<sup>34</sup>. Both are reliable, proven methods that have been commercially available for years and can measure THC concentrations (reported as equivalent parts per million methane or propane) down to the low parts per million levels. A variant on the FID method utilizes a heated ( $\approx 150^\circ\text{C}$ ) sample line, filter, and analyzer, which provides additional measurement capabilities of THC that condense out between  $150^\circ\text{C}$  and ambient temperatures. Although not required in the permit of facilities as a general rule, many facilities are equipped with THC analyzers.

### **3.3 Continuous Emission Monitors for Volatile Organic Compounds**

The real-time or near-real-time measurement of VOCs in flue and stack gases is not as well-developed a technology as is the measurement of CO and THC. The U.S. EPA has proposed draft performance specifications for the operational requirements for VOC CEMs.<sup>35,36</sup> However, several instruments at various stages of development exist and are adaptable from commercially available equipment. In 1995, the U.S. EPA held a demonstration at their pilot-scale incineration research facility in Jefferson, AK and invited instrument manufacturers to bring their instruments to the site, where the EPA paid for the operation of the facility and all sampling and analytical activities. Several manufacturers brought their instruments and attempted, with mixed results, to measure the concentrations of several target analytes in the incinerator stack gas and compare the results to standard EPA methods. Table 3-1 lists information about the various techniques for rapid measurement of VOC PICs and their approximate instrument detection limits; note that this table only includes instruments that are commercially available or are at a position in their development that would enable rapid commercial development if the market forces allowed.

Table 3-1. Techniques for Rapid Measurement of VOC PICs

Method	Target Analytes	Sampling/ Analytical Time Frame	Approximate Detection Limit	Issues	Availability
Online GC <sup>38</sup>	VOCs (up through MCBz and Cl <sub>2</sub> Bz)	<1 hour	Low ppbv	Potential for co-eluting peaks	Can be assembled from commercially available components
Ion mobility spectroscopy (IMS)	VOCs	<1 min.	Low ppbv	Low specificity	IMS for some organic compounds is available now (ETG)
Differential optical absorption spectroscopy (DOAS)	UV absorbing organic compounds	Real-time if no concentration is used; but concentration is necessary to improve detection limits	Low ppmv	Detection limits are too high	Available for some organic compounds now (ABB/OPSIS)
Fourier transform infrared (FTIR)	Some VOCs	Minutes if no concentration is used	Low ppmv	Detection limits are too high	Commercially available
Online Direct-Sample MS <sup>37,39</sup>	VOCs	1 min.	Low ppbv	May require GC to improve specificity	Can be assembled from commercially available components
REMPI <sup>25,31</sup>	Compounds with aromatic ring	Real-time if no concentration is used	Low pptv	Need spectra for each congener to be measured; may require concentration for highly halogenated compounds	Can be assembled from commercially available components

### 3.4 Continuous Emission Monitors for Chlorobenzenes and Chlorophenols

Options for rapid measurement techniques for CBz and CPh are much more limited. Other than MCBz and Cl<sub>2</sub>Bz, these compounds are in the semivolatile range of boiling points. Getting a valid stack gas sample into the instrument is not well established for all instrument types. CPh are also fairly reactive compounds and can chemisorb on surfaces.<sup>40</sup> In addition, the detection

limits for most of the instruments listed in Table 3-2 are not low enough for direct measurement of CBz and CPh—some concentration step must be performed, and there are no data in the literature for many of these instruments successfully measuring flue and stack gas CBz and CPh. Table 3-2 lists the techniques for rapidly measuring CBz and CPh. Thus far, only the variants on REMPI techniques have been successfully used for online measurements of nearly the complete set of CBz and CPh isomers.

Table 3-2. Techniques for Rapid Measurement of CBz and CPh

Method	Target Analytes	Sampling/ Analytical Time Frame	Approximate Detection Limit	Issues	Availability
Online GC <sup>38</sup>	MCBz and Cl <sub>2</sub> Bz only	<1 hour	Low ppbv	Potential for co-eluting peaks	Can be assembled from commercially available components
REMPI <sup>25,31</sup>	All isomers of Cbz and CPh	Real-time if no concentration is used	Low pptv	Need spectra for each congener to be measured; may require concentration for highly halogenated compounds	Can be assembled from commercially available components

### 3.5 Continuous Emission Monitors for Polycyclic Aromatic Hydrocarbons

A monitor for particle-bound PAH using photoelectric detection is commercially available from EchoChem. The measurement is performed on a stack slip stream that is diluted with ambient air. This instrument gives a single semi-quantitative reading representing an equivalent concentration of 2- and 3-ringed PAHs and is sensitive down to the 10 ng/dscm range. It has a very fast response time and has been used in the past to measure transient changes in emissions from a pilot-scale rotary kiln burning tire-derived fuel.

### 3.6 Continuous Emission Monitors for Lower Chlorinated Dioxins and Furans

The only instruments that have successfully demonstrated the capability of measuring lower chlorinated CDDs/Fs from combustion systems has been the REMPI-TOF and the Jet-REMPI. Due to phenomena associated with the REMPI technique, sensitivity falls off with increasing

chlorine substitution on the target molecules. As such, a concentration step may be necessary to achieve appropriate detection limits for use of this technique to the measurement of lower chlorinated CDDs/Fs.

## 4.0 Conclusions

Based on the current state-of-the-art in using surrogate indicators for measurement of PCDDs/Fs, it appears that:

1. The development of correlations between indicator compounds and PCDDs/Fs is likely to be facility-specific, although information acquired during the development of detailed regression correlations at one facility may be used successfully at other similar facilities to reduce the cost and workload of developing correlations at those facilities.
2. Sampling of the indicator compounds and PCDDs/Fs does not necessarily need to be performed at the same location to develop the correlations. Targeting sampling locations so that desired indicators are predominantly in the gas-phase can improve detection limits for trace species.
3. The ability of the surrogates to predict PCDD/F concentrations improves when a wider range of concentrations is used to develop the correlations.
4. Low MW VOC PICs may be useful as PCDD/F indicators, but some sort of temperature-related parameter should be included in the correlation to improve the fit.
5. Instrument detection limits of 1 ppbv may not be sufficient to allow for development of correlations between low MW VOCs and PCDDs/Fs.
6. In developing the facility-specific correlations between CBz/CPh and PCDDs/Fs, individual isomers as well as homologue groups and entire classes of compounds should be considered as surrogates.
7. The CBz, CPh, and low chlorinated CDDs/Fs are more effective surrogates than the low MW VOC PICs; however, their rapid measurement is more difficult.
8. Based purely on the limited available datasets, it appears that using CBz, CPh, and low chlorinated CDDs/Fs can give roughly the same ability to account for the variability in PCDD/F emissions. With the current level of information, it is not possible to definitively pick any one of these compounds as the ideal surrogate. Rather, since the concentrations of many of these compounds are likely to be cross-correlated with each other, linear combinations of all of these semivolatile compounds, derived through principal component analysis, may yield the most effective correlations.
9. Developing correlations using simultaneous measurements of CBz, CPh, and PCDDs/Fs may not meet current compliance requirements; however, it will be extremely useful to allow facilities to optimize operation to minimize PCDD/F emissions and understand the role that transient emissions play in the overall emissions of PCDDs/Fs. In addition, development of facility-specific correlations would enable a facility to estimate

bounding conditions and appropriate confidence intervals for dioxin surrogates that would assure compliance.

10. Before this technique can be used with adequate confidence at waste combustion facilities on a routine basis, additional datasets need to be generated. It would be useful to make detailed, isomer-specific measurements of CBz and CPh compounds, as well as low chlorinated CDDs/Fs, during every test where PCDDs/Fs are measured.
11. The REMPI-based instruments have shown their potential for being able to successfully measure the compounds that yield the best correlations with PCDDs/Fs. However, it is unlikely that they will be developed to be fully commercial without some sort of outside force generating a market for instrument manufacturers to enter. This force could be regulatory in nature (e.g., the EPA mandating their use) although such a requirement is not in place at this time. Rather, it may be that a forward-thinking facility or a government-operated facility may want to install one on their stack to perform system optimizations.

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16. ABSTRACT Emissions of polychlorinated dibenzo- <i>p</i> -dioxins and polychlorinated dibenzofurans (PCDDs/Fs) from stationary combustion sources are of concern because they are carcinogenic and may result in disruption of endocrine systems in human and wildlife populations. PCDDs/Fs are typically present in only minute concentrations in combustor stack gases, which makes sampling and analysis of these compounds extremely expensive and time consuming. Direct, real-time measurement of all PCDD/F isomers of concern is not possible using current technology. However, it is possible to estimate stack PCDD/F concentrations by measuring other indicator (surrogate) compounds that are present in the stack gases at much higher concentrations. These appropriately selected surrogate compounds would be easier to measure than PCDDs/Fs, and could be measured in real-time or near real-time by stack gas monitoring technology that is currently available either commercially or that is in various stages of development. The report discusses the various surrogates that can be used to indicate PCDD/F concentrations, how those surrogates can be measured, and a state-of-the-art assessment of availability and effectiveness of analyzers for measuring those compounds.		
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